

Supporting Information for:

Noncovalent immobilization of electrocatalysts on  
carbon electrodes for fuel production

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## Materials and Methods Section

### General

4,4'-Dimethyl-2,2'-bipyridine (GFS Chemicals), sulfuric acid (J.T. Baker), potassium dichromate, thionyl chloride and 1-Pyrenemethylamine hydrochloride (Sigma-Aldrich) were used as received. Acetonitrile (J.T. Baker) was dried using a Grubbs-type solvent purification system (Pure Process Technology/Glass Contour). 2,2'-Bipyridine-4,4'-dicarboxylic acid,<sup>1</sup> [Cp\*RhCl<sub>2</sub>]<sub>2</sub>,<sup>2</sup> [Cp\*Rh(phen)Cl]Cl (**3**),<sup>3</sup> and Re(bpy)(CO)<sub>3</sub>Cl (**4**)<sup>4</sup> were prepared according to the literature. NMR spectra were recorded at room temperature on 300 or 500 MHz Varian spectrometers and referenced to the residual solvent peak ( $\delta$  in ppm and  $J$  in Hz). Mass spectra were obtained with a PE SCIEX API 365 triple quadrupole spectrometer.

**N<sup>4,4'</sup>-bis(1-pyrenylmethyl)-[2,2'-dipyridyl]-4,4'-dicarboxamide (P)**. The acid chloride of 2,2'-bipyridine-4,4'-dicarboxylic acid was prepared by refluxing 0.37 g (1.5 mmol) of the bipyridine-carboxylic acid in 15 mL of neat thionyl chloride for 8 h. Remaining thionyl chloride was removed under vacuum. In a separate flask, 0.8 g (3 mmol) of 1-pyrenemethylamine hydrochloride were combined with 150 mL of dry acetonitrile and 0.9 mL of 1,8-diazabicyclo[5.4.0]undec-7-ene (ca. 4 equivalents). The resulting solution was transferred to the solid bipyridine-acid chloride via cannula. The mixture was stirred for 12 h at room temperature, at which time 20 mL of saturated sodium bicarbonate and 130 mL deionized water were added to form a beige precipitate. The precipitate was collected using vacuum filtration and washed three times with 10 mL portions of deionized water. The precipitate was dried under vacuum to give 0.85 g (85%) of an off-white solid. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  5.26-5.28 (d,  $J$ = 5.27Hz, 4H), 8.05-8.17 (m, 9H), 8.26-8.32 (m, 9H), 8.49-8.52 (d,  $J$ = 8.51Hz, 2H), 8.83-8.85 (d,  $J$ = 8.84Hz, 2H), 8.85 (s, 2H), 9.72 (s, 2H). <sup>13</sup>C NMR (126 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  164.6, 155.5, 150.1, 142.7, 132.4, 130.8, 130.3, 130.2, 128.2, 127.7, 127.4, 127.1, 127.0, 126.3, 125.3, 125.2, 124.8, 124.1, 123.9, 123.2, 122.1, 118.3, 41.3. ESI-MS (positive)  $m/z$ : found 671.3 (**1** + H<sup>+</sup>).

**[( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Rh(N<sup>4,4'</sup>-bis(1-pyrenylmethyl)-[2,2'-dipyridyl]-4,4'-dicarboxamide)Cl]Cl (**1**)** A portion of [Cp\*RhCl<sub>2</sub>]<sub>2</sub> (100 mg, 0.162 mmol) was dissolved in 20 mL of acetonitrile. A portion of **P** (150 mg, 0.338 mmol) was added to this solution, and following reflux for 24 hours at 60°C under argon, a yellow precipitate formed. The precipitate was filtered, and the solid redissolved in dichloromethane and filtered once more. A portion of diethyl ether was added to precipitate the product, which was then collected and dried under vacuum. <sup>1</sup>H NMR (300MHz, DMSO-*d*<sub>6</sub>)  $\delta$  1.64 (s, 15H), 5.30-5.32 (d, 4H) 8.05-8.17 (m, 9H), 8.24-8.32 (m, 9H), 8.46-8.49 (d, 2H), 9.10-9.12 (d, 2H), 9.13 (s, 2H), 9.96 (s, 2H). <sup>13</sup>C NMR (126 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  162.8, 154.3, 153.0, 144.3, 131.9, 130.8, 130.30, 130.26, 128.2, 127.8, 127.4, 127.2, 126.9, 126.4, 126.3, 125.4, 125.3, 124.8, 124.1, 123.9, 123.2, 121.7, 97.4 (d,  $J$ =25 Hz, Cp\* ring), 41.5, 8.4 (Cp\* methyl). ESI-MS (positive)  $m/z$ : found 943.3 (**2** – Cl<sup>-</sup>).

**fac-(N<sup>4,4'</sup>-bis(1-pyrenylmethyl)-[2,2'-dipyridyl]-4,4'-dicarboxamide)tricarbonylchloro rhenium(I) (**2**)** [Re(CO)<sub>3</sub>Cl] (.50 g, .138 mmol) was dissolved in 20 mL of toluene. To this solution, a portion of **P** (.83g, .187 mmol) was added. After refluxing for 24 hours at 110°C under argon, the solution was filtered to give an orange solid. The solid material was redissolved in THF before being filtered once more to remove free **1**. The solution was then concentrated by rotary evaporation. 30 mL of diethyl ether was added to the solution and the product was filtered off as an orange precipitate. The precipitate was then collected and dried under vacuum before being stored. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  5.32-5.34 (d,  $J$ = 5.33Hz, 4H) 8.07-8.18 (m,  $J$ = 5.27Hz, 9H), 8.26-8.33 (m, 9H), 8.46-8.49 (d,  $J$ = 8.48Hz, 2H), 9.13 (s,

2H), 9.18-9.20 (d,  $J = 9.19\text{ Hz}$ , 2H), 9.92 (s, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  163.1, 155.7, 153.8, 144.3, 131.8, 130.8, 130.3, 130.3, 128.3, 127.8, 127.4, 127.3, 126.9, 126.4, 125.8, 125.4, 125.4, 124.8, 124.1, 123.9, 123.1, 122.4, 41.5. ESI-MS (positive)  $m/z$ : found 941.2 ( $3 - \text{Cl}^-$ ).

### Carbon electrode preparation

Blocks of highly-oriented pyrolytic graphite (HOPG) carbon (GraphiteStore.com, Buffalo Grove, Ill.) were cleaned by sanding the basal plane with 600 grit silicon carbide paper, followed by sonication in water and methanol for 30 min each. The blocks were then rinsed with an additional portion of methanol before drying in air.

A suspension of Ketjen black was prepared by grinding 40 mg of the commercial material (EC600JD, AkzoNobel) with a mortar and pestle. The resulting powder was then combined with 5 mL *N*-methylpyrrolidone, 10 mg poly(vinylidene fluoride) (Sigma-Aldrich), and 0.75 g of Triton-X 100 and sonicated for 3 hours (VWR Aquasonic 150D).

To deposit the carbon black on the clean basal-plane surface of HOPG, the surface was first wet with acetonitrile, and then  $10\text{ }\mu\text{L per cm}^2$  of the carbon black suspension was added via pipette. The electrode was allowed to dry in ambient air for 15 min before transferring to an oven at  $70^\circ\text{C}$  for 4 hours.

### X-ray photoelectron spectroscopy

XP data were collected using a Kratos AXIS Ultra system. The sample chamber was kept at  $<5 \times 10^{-9}$  torr and ejected electrons were collected at an angle of  $90^\circ$  from the surface normal. Survey scans were performed to identify the elements on the surface of the carbon electrodes, while additional high-resolution spectra were obtained for details on specific elements.

The XPS data were analyzed using the program Computer Aided Surface Analysis for X-ray Photoelectron Spectroscopy (CasaXPS). All XPS signals reported here are binding energies and are reported in eV. Backgrounds were fit with standard Shirley or linear backgrounds, except for the case of the Rh 3d region, which required a linear spline function. Element peaks were fit with a standard Gaussian-Lorentzian line shape. For the Rh and Re high-resolution spectra, the data were best fit with a single contribution in every case, and fits were constrained only based on peak FWHM. This resulted in reasonable agreement with expected peak area ratios.

### Electrochemistry

Electrochemical measurements were made with a Gamry Reference 600 potentiostat/galvanostat using a standard three-electrode configuration. For all experiments, the supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate (Fluka, electrochemical grade). In the case of electrochemical studies with immobilized compounds, the electrolyte solvent was acetonitrile. In the case of solution-soluble compounds, the electrolyte solvent was acetonitrile or dichloromethane as noted.

In typical cyclic voltammetry measurements of immobilized complexes, the working electrode consisted of a  $1\text{ cm}^2$  block of HOPG prepared with carbon black on the basal plane as described above. The electrode was secured in a custom-made Teflon cell with an O-ring seal used to define the geometric area of the electrode ( $0.28\text{ cm}^2$ ). The counter electrode was a Pt wire, and a silver wire immersed in a solution of 0.1 M  $\text{NBu}_4\text{PF}_6$  served as a quasi-reference electrode. This quasi-reference was separated

from the main working solution by a Vycor frit (Bioanalytical Systems, Inc.). The ferrocenium/ferrocene couple was used as an external reference in all experiments to calibrate potentials.

Voltammetry collected for solution-soluble redox couples was obtained at a basal-plane HOPG working electrode (surface area:  $0.09\text{ cm}^2$ ). A Pt wire served as the counter electrode, with a  $\text{Ag}/\text{Ag}^+$  reference as described above. Concentrations were typically  $10^{-3}\text{ M}$ . The surface was prepared according to a previous report.<sup>5</sup>

Controlled-potential electrolysis coupled to product detection was carried out with a standard three-electrode configuration in a custom two-compartment air-tight cell. The working electrode consisted of a ca.  $10\text{ cm}^2$  block of HOPG prepared with carbon black as described above. The reference and counter electrodes were as described above. The volume of solution held by the cell in total was 70 mL, with ca. 100 mL of total headspace volume.

In a typical experiment for hydrogen gas detection, the cell was prepared in a nitrogen-filled glovebox with a 5 mM tosic acid solution in electrolyte. Following 1.25 hr of electrolysis, headspace gas was analysed for dihydrogen content. No other reduction products were detected.

In a typical experiment for CO gas detection, the cell was prepared in a nitrogen-filled glovebox with electrolyte. Then, the cell was removed from the glovebox and purged with  $\text{CO}_2$  for 45 minutes before initiation of electrolysis. Following 1.25 hr of electrolysis, headspace gas was analyzed for CO content.  $\text{CO}_2$  is the source of CO produced; bulk electrolysis using an electrode prepared with rhenium catalyst **2** but no headspace  $\text{CO}_2$  gas does not produce CO.

Total turnover numbers were calculated based on surface loading of catalyst obtained from integration of cyclic voltammograms collected in the absence of substrate prior to beginning the electrocatalytic runs with added  $\text{H}^+$  or  $\text{CO}_2$ .

## Gas chromatography

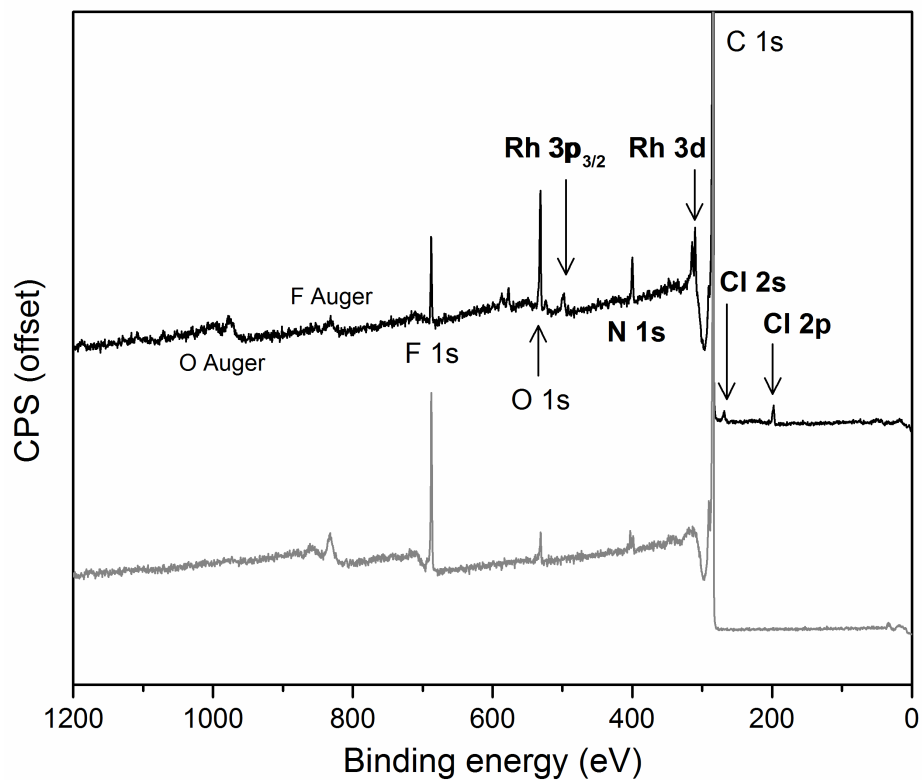
Gas analysis for the controlled-potential electrolyses was performed with an Agilent 7890A gas chromatograph with separate columns for analysis of hydrogen gas and nitrogen, oxygen, carbon dioxide, carbon monoxide, hydrogen disulfide, methane, ethane, ethylene, and ethyne. Each column was calibrated with standard gas mixtures to obtain quantitative data.

Minimal oxygen was detected in the headspace samples. As expected, large quantities of nitrogen and carbon dioxide were found in the runs for hydrogen production and CO production, respectively.

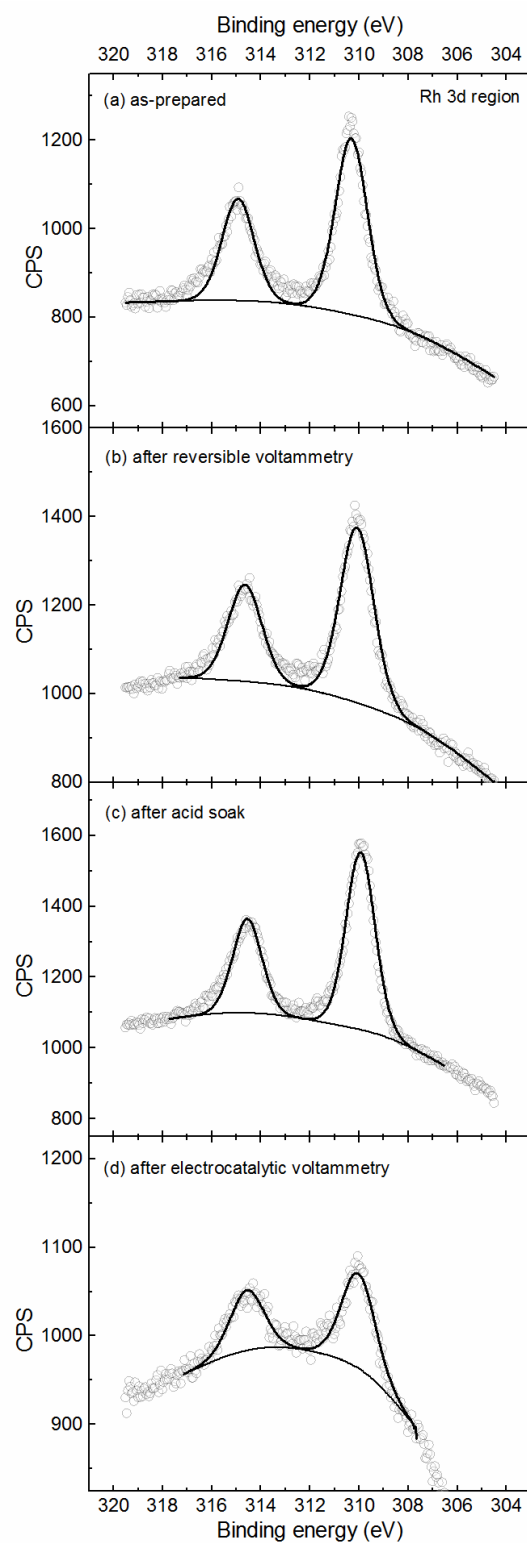


## Supplementary Figures

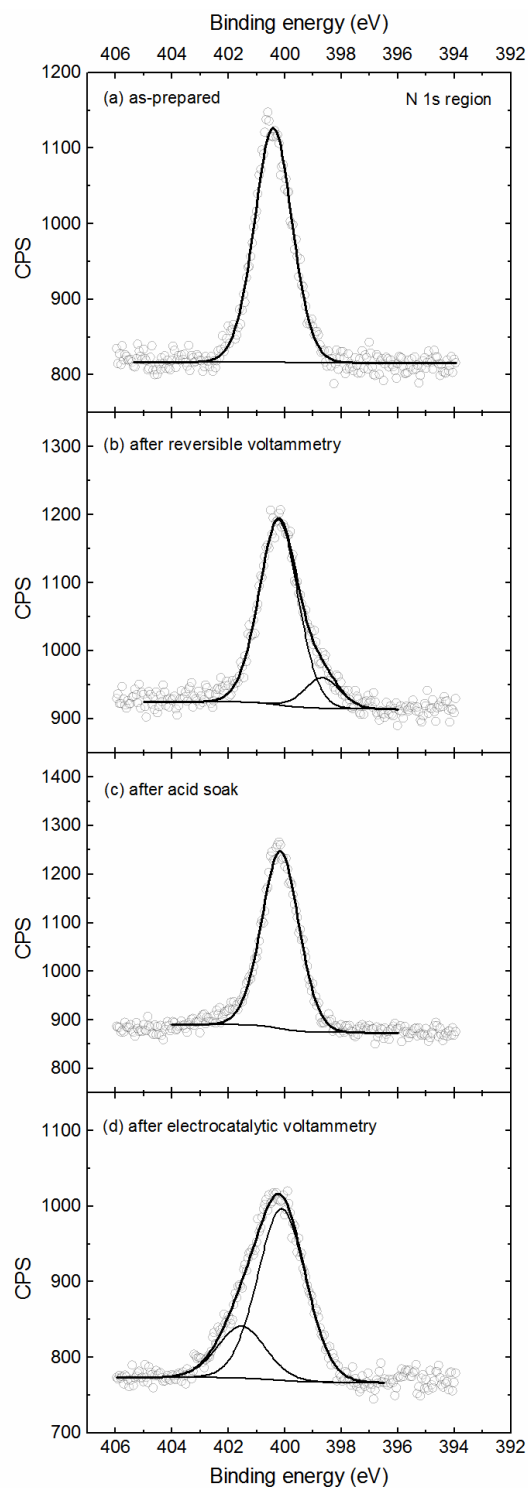
**Figure S1.** XP survey spectra for blank carbon electrode (gray line) and **1** immobilized on carbon electrode (black line).



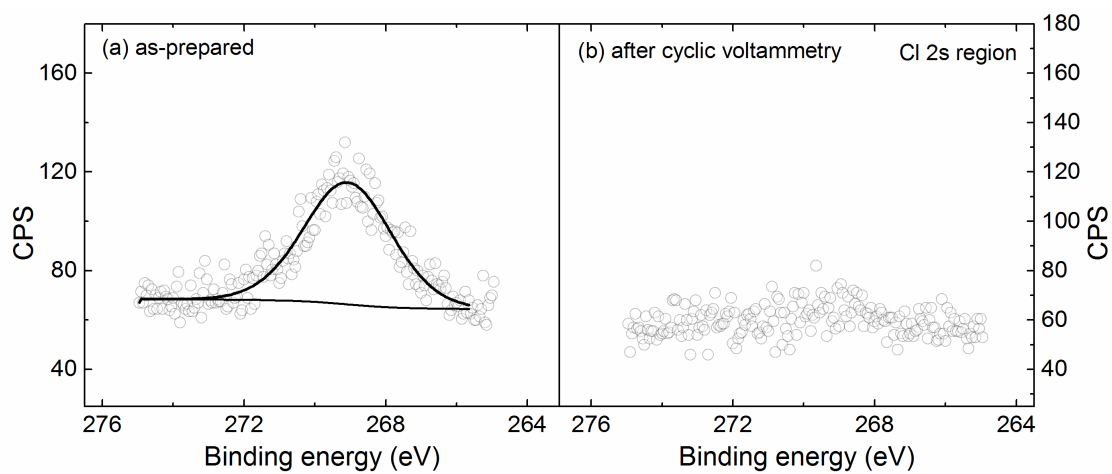
**Figure S2.** Rh 3d XP spectra for **1** immobilized on carbon electrode. (a) Electrode as-prepared; (b) after reversible cyclic voltammetry; (c) after soaking in tosic acid for 1 hr; (d) after catalytic voltammetry.



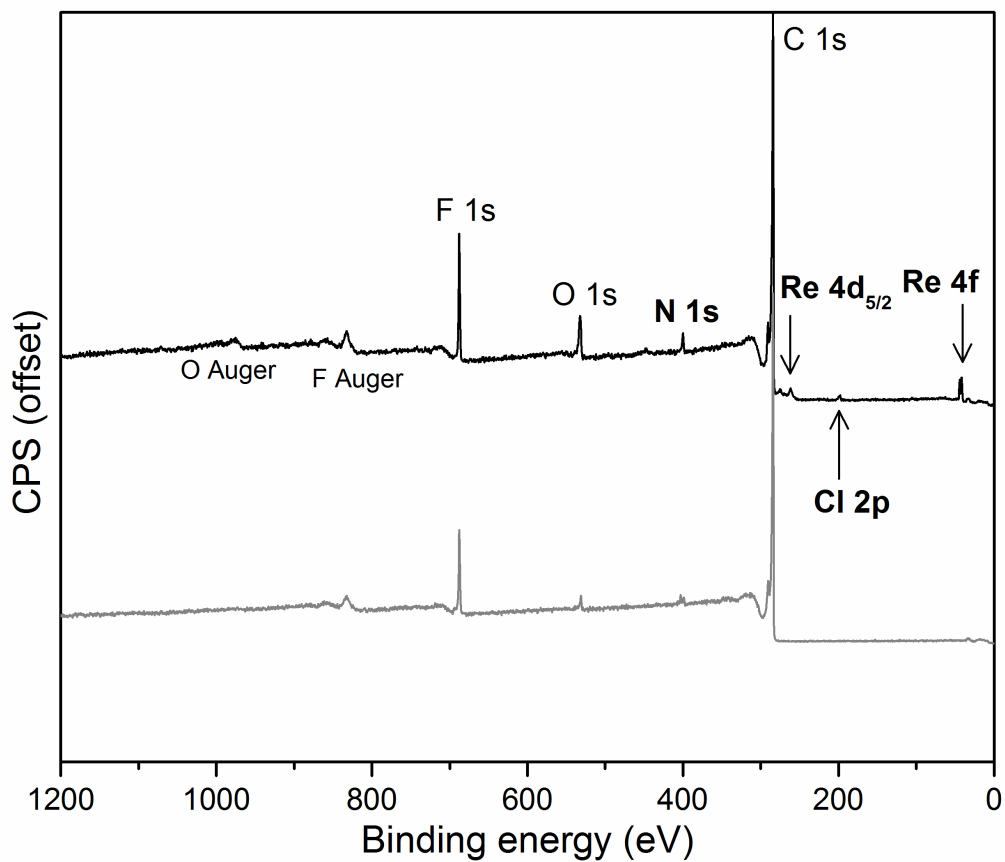
**Figure S3.** N 1s XP spectra for **1** immobilized on carbon electrode. (a) Electrode as-prepared; (b) after reversible cyclic voltammetry; (c) after soaking in tosic acid for 1 hr; (d) after catalytic voltammetry.



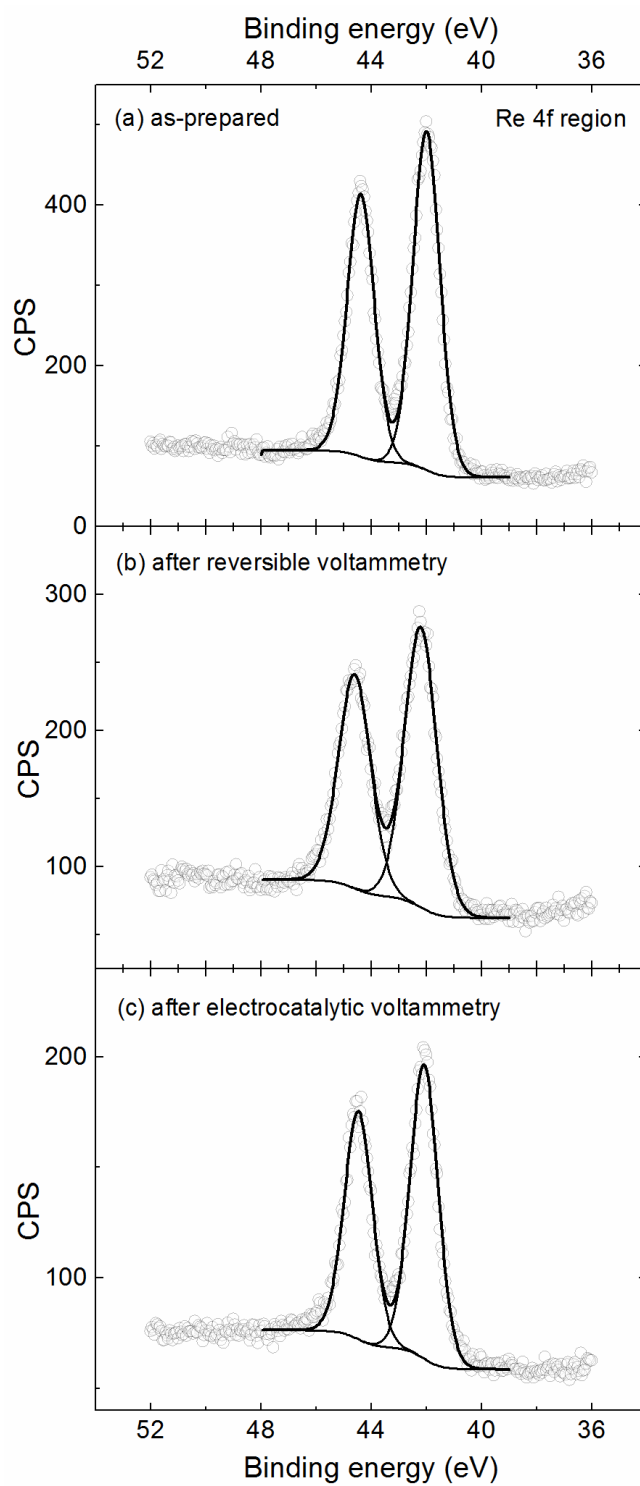
**Figure S4.** Cl 2s XP spectra for **1** immobilized on carbon electrode. (a) Electrode as-prepared; (b) after reversible cyclic voltammetry.



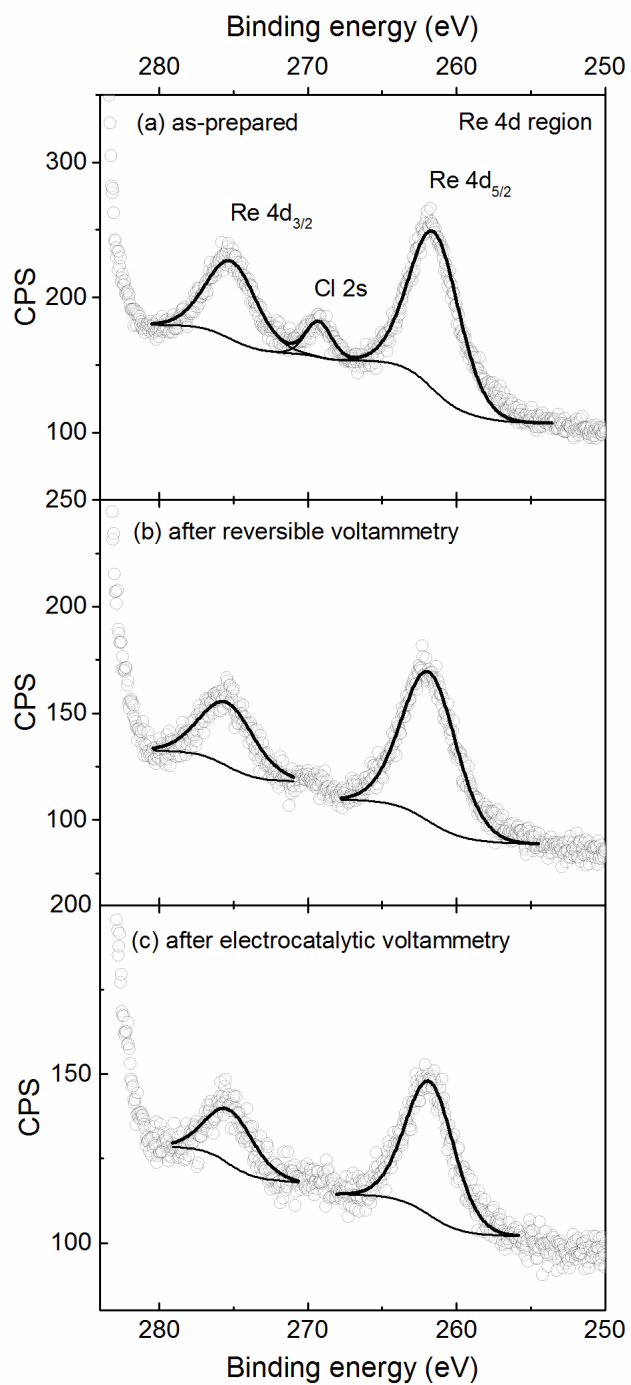
**Figure S5.** XP survey spectra for blank carbon electrode (gray line) and **2** immobilized on carbon electrode (black line).



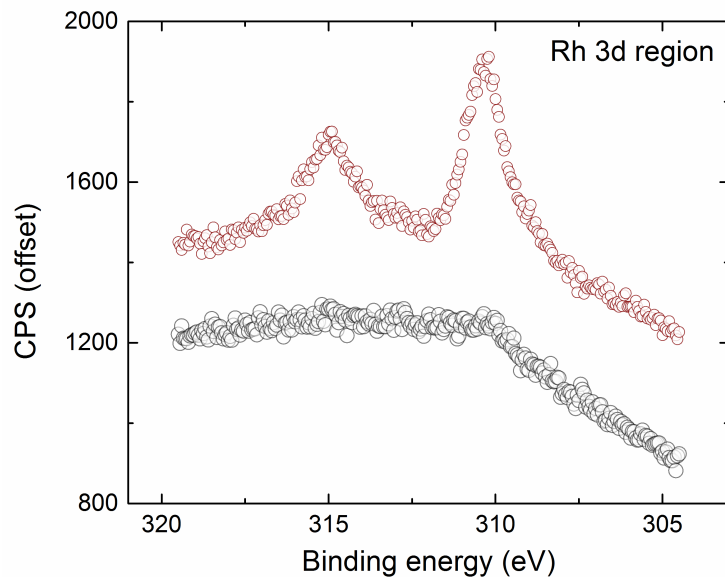
**Figure S6.** Re 4f XP spectra for **2** immobilized on carbon electrode. (a) Electrode as-prepared; (b) after reversible cyclic voltammetry; (c) after electrocatalytic voltammetry.



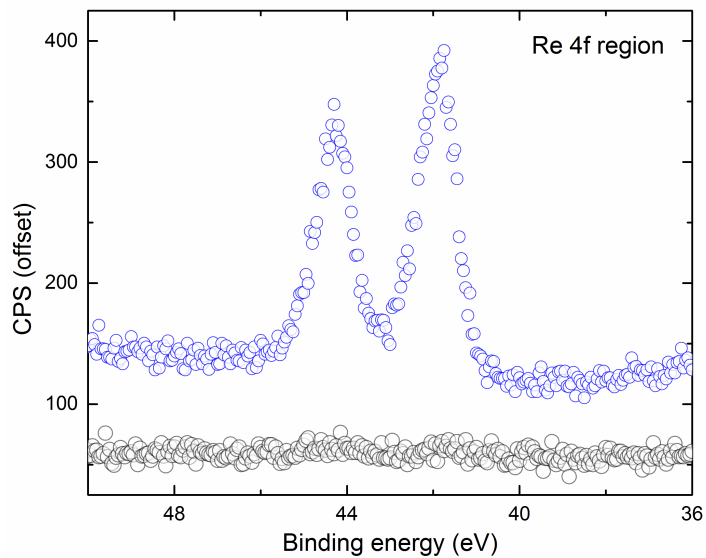
**Figure S7.** Re 4d and Cl 2s XP spectra for **2** immobilized on carbon electrode. (a) Electrode as-prepared; (b) after reversible cyclic voltammetry; (c) after electrocatalytic voltammetry.



**Figure S8.** Comparison of Rh 3d XP spectra for carbon electrodes soaked in **1** (red circles) or **3** (gray circles) followed by soaking in acetonitrile to remove complexes not strongly bound. No Rh is visible on the electrode for the case of **3**.

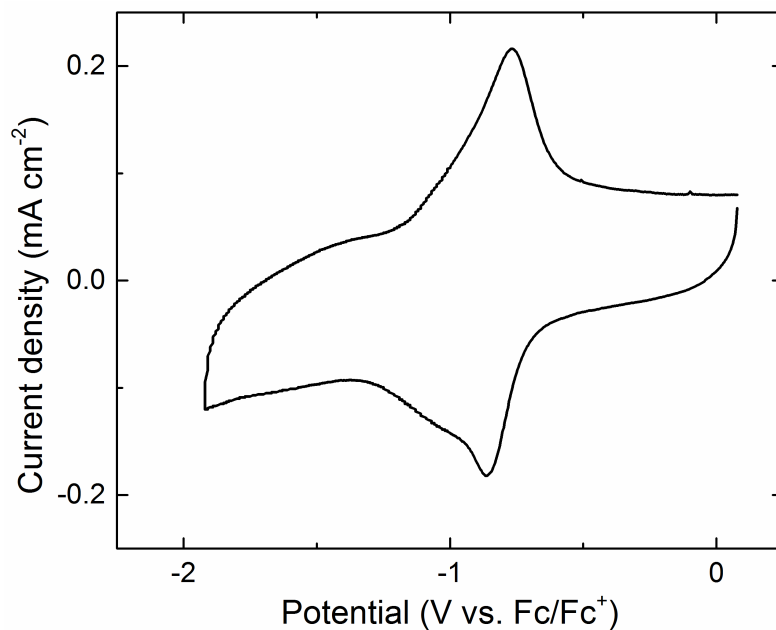


**Figure S9.** Comparison of Re 4f XP spectra for carbon electrodes soaked in **2** (blue circles) or **4** (gray circles) followed by soaking in acetonitrile to remove complexes not strongly bound. No Re is visible on the electrode for the case of **4**.

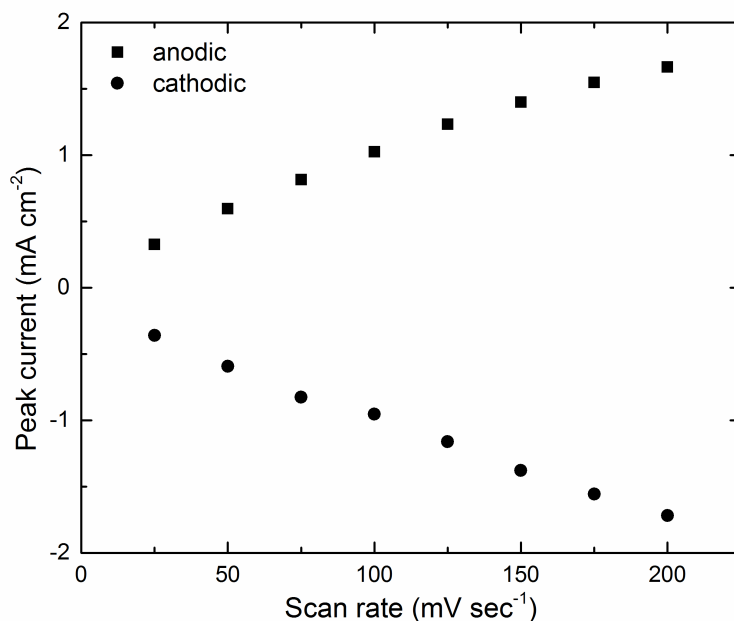




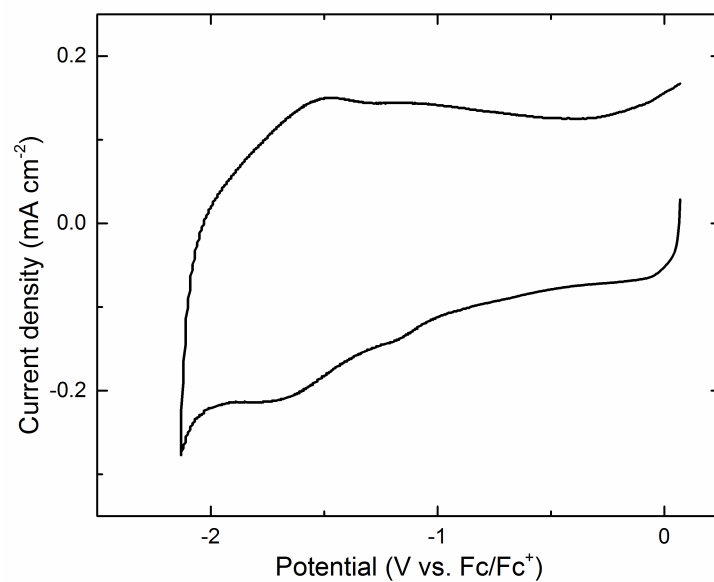
**Figure S10.** Cyclic voltammograms of immobilized **1** at a scan rate of 10 mV/s. Peak-to-peak separation here is 104 mV (vs. 495 mV at 150 mV/s). Integration of the peak area (background subtracted) shows ca. 1.2 ( $\pm 0.1$ ) mC transferred upon reduction, and 1.4 mC transferred upon re-oxidation, corresponding to a reasonable reversibility of >85% based on charge re-collection.



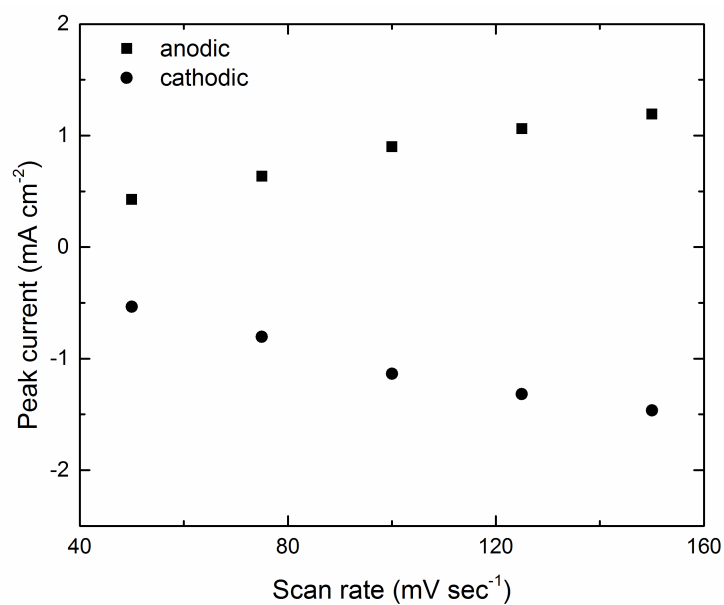
**Figure S11.** Dependence of peak currents (from cyclic voltammetry) for immobilized **1** versus scan rate. The linear dependence indicates a non-diffusional surface-bound redox process. The electrolyte solution is 0.1 M NBu<sub>4</sub>PF<sub>6</sub>.



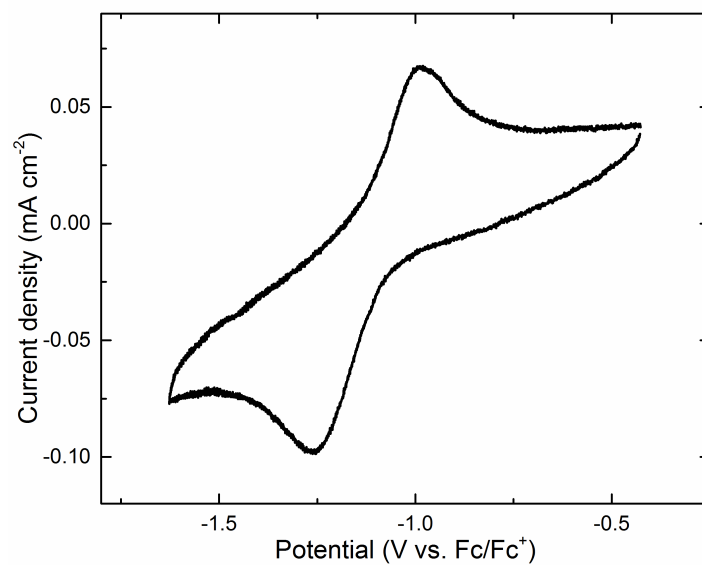
**Figure S12.** Cyclic voltammograms of immobilized **P**. The compound was immobilized by soaking the electrode in a DMSO solution of **P** for 12 hours.



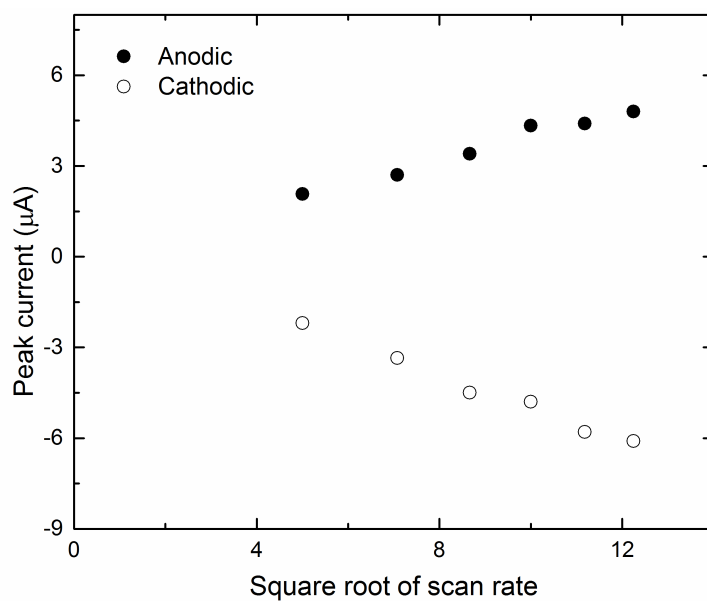
**Figure S13.** Dependence of peak currents (from cyclic voltammetry) for immobilized **2** versus scan rate. The linear dependence indicates a non-diffusional surface-bound redox process.



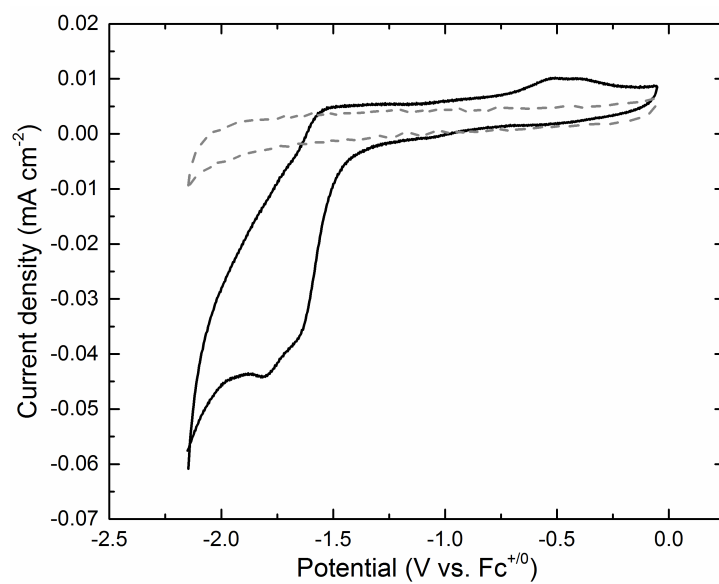
**Figure S14.** Cyclic voltammetry of **1** dissolved in dichloromethane containing 0.1 M tetrabutylammonium hexafluorophosphate at 100 mV/s.  $E_{1/2} = -1124$  mV.  $\Delta E_p = 273$  mV.



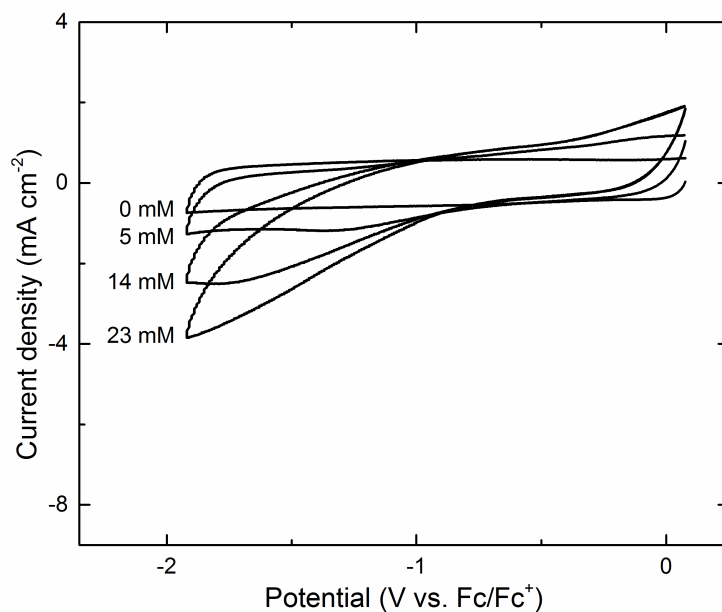
**Figure S15.** Dependence of peak currents (from cyclic voltammetry) for **1** in dichloromethane solution as in Figure S14 versus the square root of the scan rate. The linear dependence indicates a diffusional redox process.



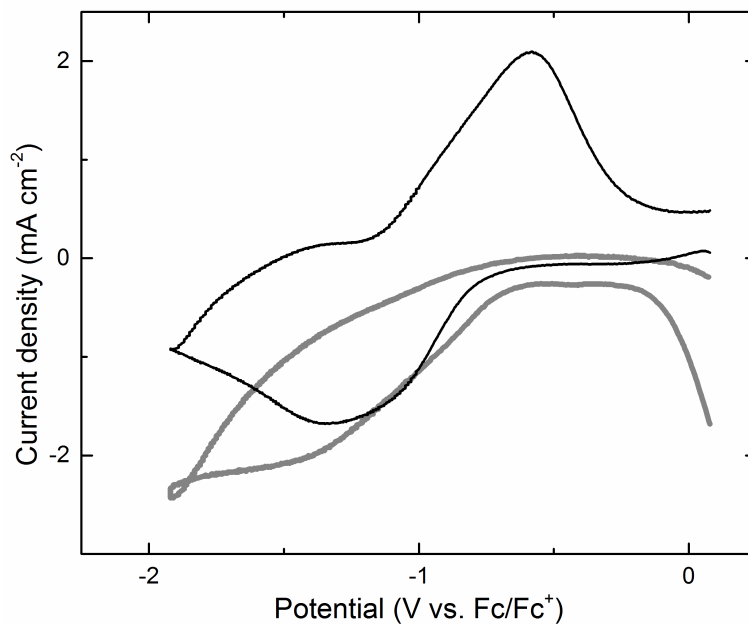
**Figure S16.** Cyclic voltammetry of **2** dissolved in dichloromethane containing 0.1 M tetrabutylammonium hexafluorophosphate. Reduction peaks are visible at -1.7 V, -1.84 V, and -2.1 V, and return anodic features are visible at -0.5 V. Scan rate: 100 mV/s.



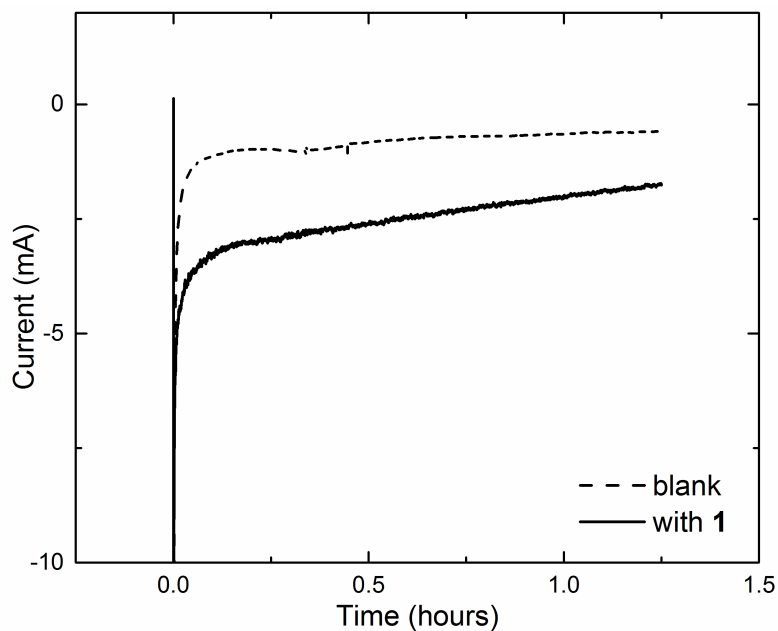
**Figure S17.** Cyclic voltammograms for a carbon electrode in the presence of increasing concentrations of toxic acid. Acid concentrations are indicated with their respective voltammograms. Currents are notably lower than in the presence of immobilized **1** (see Figure 5 in main text).



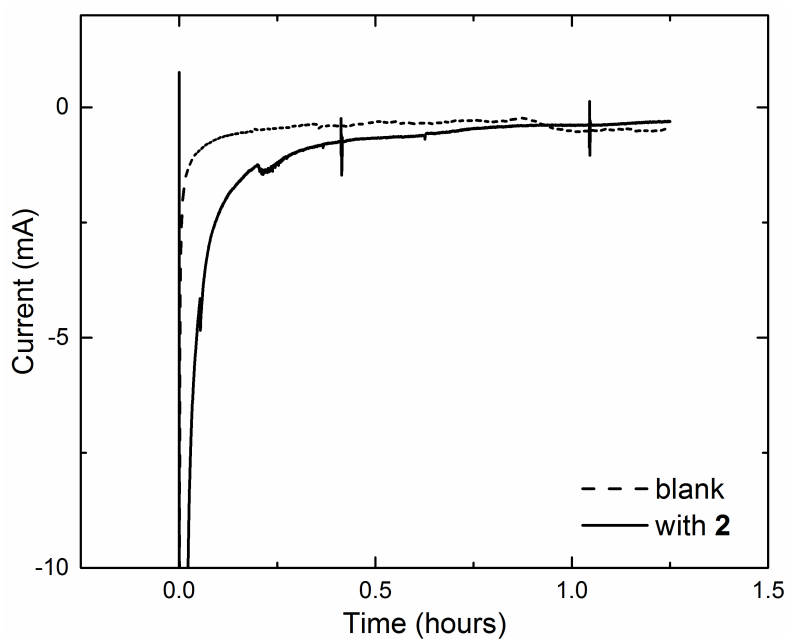
**Figure S18.** Background-subtracted cyclic voltammograms for an electrode prepared with immobilized **1** in the absence and presence of 14 mM toxic acid. Based on the surface catalyst loading from voltammetry and the catalytic current, we find a turnover frequency of  $0.95 \text{ sec}^{-1}$ .



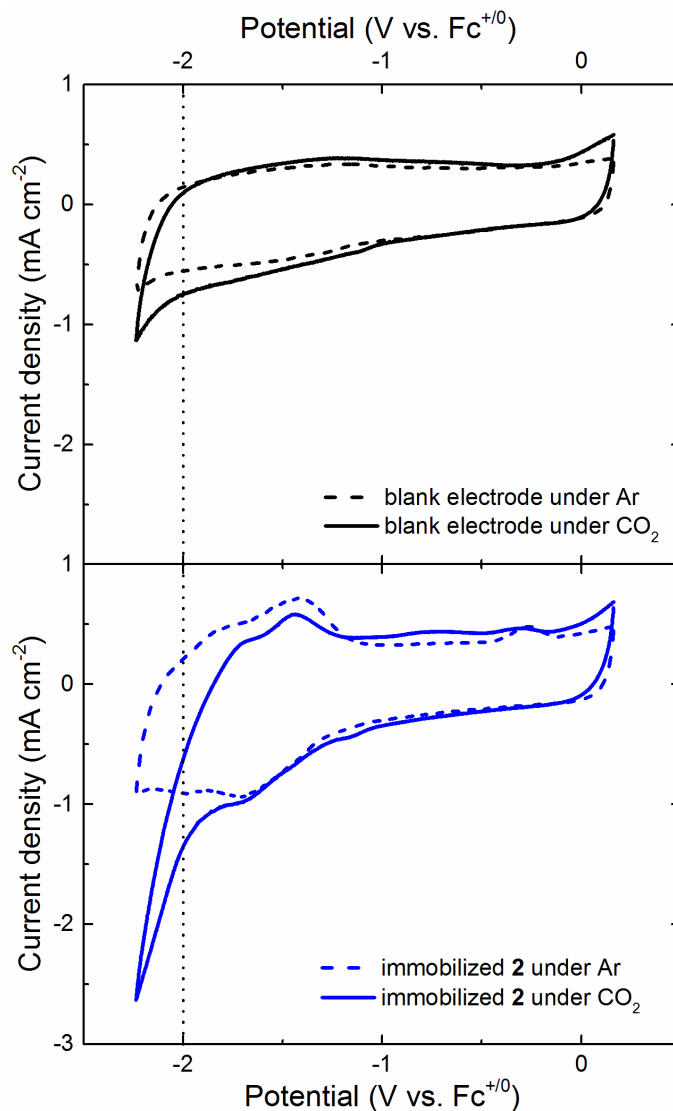
**Figure S19.** Steady state current densities during the controlled-potential electrolysis of a blank carbon electrode (dashed line) and an electrode prepared with **1** (solid line). Currents with immobilized **1** remain above background throughout the 1.25 hr electrolysis.



**Figure S20.** Steady state current densities during the controlled-potential electrolysis of a blank carbon electrode (dashed line) and an electrode prepared with **2** (solid line) under an atmosphere of CO<sub>2</sub>. Currents with immobilized **2** drop to background levels at an elapsed time of ca. 1 hr.



**Figure S21.** Comparison of cyclic voltammetric responses of electrodes prepared without **2** (upper panel) and with **2** (lower panel). Dashed black line: blank electrode under Ar. Solid black line: blank electrode under CO<sub>2</sub>. Dashed blue line: **2** under Ar. Solid blue line: **2** under CO<sub>2</sub>. Vertical dotted black line is only to guide the eye, and marks -2.0 V on both panels. Conditions: 0.1 M tetrabutylammonium hexafluorophosphate in MeCN; scan rate: 100 mV/s.



## References

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